

III.A.17 Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells (SOFCs)

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Objectives

- To develop mechanism-based evaluation procedures for the stability of SOFC interconnect materials and to use these procedures to study and modify a group of alloys which have already been identified as candidate interconnect materials, i.e. ferritic stainless steels.
- To study fundamental aspects underlying the thermomechanical behavior of interconnect materials and develop accelerated testing protocols.
- To investigate the potential for the use of “new” metals as interconnect materials.

Approach

- Characterize exposed fuel cell interfaces.
- Study and attempt to control growth rates of chromia scales on Cr and ferritic alloys.
- Study the adhesion of chromia scales subjected to cyclic oxidation conditions in simulated fuel cell atmospheres.
- Investigate evaporation of Cr-oxide species both theoretically and experimentally.
- Measure stresses in oxide scales on ferritic alloys using x-ray diffraction (XRD).
- Perform indentation testing to evaluate interface adhesion of thermally grown oxide scales and deposited coatings.
- Develop a mechanism-based, accelerated testing protocol for evaluating the thermomechanical stability of oxides and coatings on metallic interconnects.
- Evaluate the possibility of reducing the oxidation rate of pure Ni.
- Evaluate the use of Fe-Ni alloys with low coefficient of thermal expansion (CTE) (Invar) as interconnects.
- Evaluate the use of coatings to limit oxide evaporation from chromia-forming interconnect alloys.

Accomplishments

- Characterized the oxidation behavior of a variety of ferritic stainless steels in simulated fuel cell atmospheres over the temperature range 700°-900°C.

- Discovered that exposure under some fuel cell operating conditions can promote sigma phase formation in some ferritic stainless steels.
- Adapted an indentation technique for measuring interfacial fracture toughnesses for oxides formed on interconnects and for coatings applied to interconnects.
- Used interfacial toughnesses measured in specimens subjected to short exposure times to estimate times for spontaneous spallation (failure) of chromia scales.
- Ascertained that it may be possible to modify the surface of pure nickel or to alloy Ni to allow its use as an intermediate-temperature interconnect material.

Future Directions

- Evaluate the oxidation behavior of ferritic stainless steels under dual atmosphere conditions, with one side of the specimen exposed to a simulated fuel cell cathode gas and the other side exposed to a simulated anode gas.
- Continue the development of indentation as an accelerated testing technique for chromia scales and deposited coatings.
- Continue the study of coatings to reduce oxide evaporation from chromia-forming alloys.
- Investigate Cr-free alloys as possible interconnect materials.

Introduction

Solid oxide fuel cells provide a potential way to generate electricity with high efficiency and low pollution. The operating principles of fuel cells have been known for over 100 years, and low-temperature fuel cells provided the electric power on all the Gemini and Apollo spacecraft. However, fuel cells have not achieved widespread commercial use for a number of economic and technical reasons.

One of the most important technical challenges for solid oxide fuel cells, which operate in the temperature range 700°-900°C, is the design of interconnects (current collectors). These components, in addition to electrically connecting individual cells in a stack, must separate the anode compartment of one cell from the cathode compartment of the adjacent cell. This means that one side of an interconnect is exposed to the fuel, typically hydrogen or hydrocarbons in which the oxygen partial pressure is low, and the other side is exposed to the oxidant, which is typically air

Interconnect material requirements include a variety of physical, chemical, and electrical properties. The optimal interconnect material would have the following properties:

1. Low electrical resistivity.

2. Impermeability to anode and cathode gases.
3. Stability in both anode and cathode gases under thermal cycling conditions.
4. Chemical compatibility with other cell components.
5. Close match in coefficient of thermal expansion with other components.
6. Good mechanical properties.
7. High thermal conductivity.
8. Ease of fabrication.
9. Low cost.

Ceramic interconnects usually have favorable values of properties 2, 3, 4, and 5. However, they are usually deficient in the other desired properties.

Metallic interconnects are attractive in that they have favorable values of properties 2, 6, 7, 8, and 9. With respect to property 7, although metallic materials have low electrical resistivity, they react with SOFC gases to form oxide layers, which generally have high electrical resistivity. Interconnect system resistance can be greatly increased by oxide layer thickening and spallation. Oxidation-resistant alloys are designed to form one of three protective oxides: alumina, silica, or chromia. Of these, the electrical resistivities of alumina and silica are much too high for interconnect applications.

Approach

The project consists of three major tasks aligned with its three objectives.

Task 1: Mechanism-based Evaluation Procedures

A variety of chromia-forming interconnect alloys are being subjected to thermal cycling in air, in simulated anode gas ($\text{Ar-H}_2\text{-H}_2\text{O}$) and with simultaneous exposure to air on one side and simulated anode gas on the other. Combined exposures have been shown at Pacific Northwest National Laboratory (PNNL) to often yield different behavior than exposures with the same gas on both sides of the specimen. Exposure temperatures range from 700°C to 900°C . Oxidation kinetics are being tracked by mass change measurements, and corresponding changes in oxide scale resistances are being measured. Exposed specimens are being examined in cross-section by scanning electron microscopy (SEM) to document changes in structure with exposure.

Methods are being studied to slow the growth of chromia scales on Cr and ferritic alloys with exposure in order to decrease the contribution of the scale to interconnect resistance. The ability of chromite coatings to reduce harmful CrO_3 evaporation from chromia-forming interconnect alloys is also being investigated. Specimens for this task and tasks 2 and 3 are being provided by PNNL, the National Energy Technology Laboratory (NETL) and Solid State Energy Conversion Alliance (SECA) Industrial Team members.

Task 2: Fundamental Aspects of Thermomechanical Behavior

Understanding the resistance of growing chromia scales to spallation requires a fundamental understanding of the mechanics of chromia adhesion. From a fracture mechanics standpoint, the adherence of protective oxide scales to alloy substrates is governed by 1) the stored elastic energy in the scale, which drives delamination, and 2) the fracture toughness of the alloy/oxide interface, which quantifies the resistance to fracture.

The stored elastic energy in the scale is increased by increases in the scale thickness (which can be

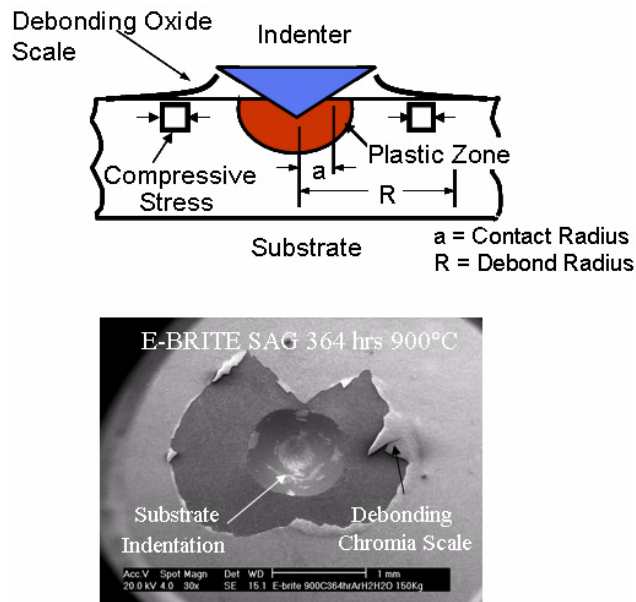


Figure 1. Indentation Fracture Testing Techniques Used to Study the Thermomechanical Behavior of SOFC Interconnects

measured by cross-section SEM) and increases in the residual stress in the scale. In this task, x-ray diffraction (XRD) is being used to measure stresses in chromia films formed on pure chromium and chromia-forming alloys after the exposures described for Task 1.

An indentation test (see Figure 1) is also being used to measure the fracture toughness of chromia/alloy interfaces for the same exposures. In the test, the chromia scale is penetrated by the indenter, and the plastic deformation of the underlying substrate induces compressive radial strains in the substrate. These strains are transferred to the coating, and the associated coating stress drives the extension of a roughly axisymmetric interface crack. The interfacial toughness can be determined from the results of a mechanics analysis of the indentation problem and a measurement of the delamination radius.

SOFCs must be able to operate for very long periods of time (e.g. 40,000 h with hundreds of thermal cycles). Clearly, testing interconnect alloy modifications over this time period is not feasible, and accelerated testing protocols are needed. In addition to subjecting specimens to exposures at higher temperatures and increasing thermal cycle frequency, XRD and indentation are being used as

accelerated testing techniques, yielding insight into scale durability after short exposure times.

Task 3: Alternative Material Choices

Metallic materials other than chromia-formers are being considered for use as low-temperature SOFC interconnects. Experiments similar to those described for Task 1 are being performed on pure Ni. Its only oxide, NiO, has no vapor species with high partial pressures, and it has a higher electrical conductivity than chromia. NiO should not even form in the anode gas. In addition, low-CTE, dispersion-strengthened Ni is being considered. The alternatives being considered are dispersing Y_2O_3 or Li_2O in Ni. The latter would also provide a potential source of Li^{+1} cations to dope the NiO scale.

Low-CTE Fe-Ni alloys (Invar) are also being considered. Because the CTE of Invar is substantially lower than that of typical ceramic SOFC components, increasing Ni content may be needed allow the interconnect CTE to be matched to that of SOFC ceramic components. Neither component of these alloys will form oxide in the anode gas. Evaporation of CrO_3 can be reduced by the use of coatings, as described above. This concept is also being pursued.

Results

Task 1: Mechanism-based Evaluation Procedures

The cyclic oxidation of three ferritic stainless steels has been evaluated under conditions pertinent to fuel cell operation. The alloys are (compositions in wt%):

- E-BRITE (Fe-26 Cr-1 Mo-0.2 Si)
- AL 453 (Fe-22 Cr-0.6 Al-0.3 Mn + 0.1Ce/La)
- Crofer (Fe-22Cr-0.5Mn-0.08 Ti-0.016P-0.06 La)

Cycle times of 1 hour were used, with exposure temperatures of 700°C and 900°C. The exposure environments included

- Dry Air (Simulated Cathode Gas)
- Air + 0.1 atm H_2O
- Ar/ H_2 / H_2O (Simulated Anode Gas) ($P_{O_2} = 10^{-17}$ atm at 900°C and 10^{-20} atm at 700°C)

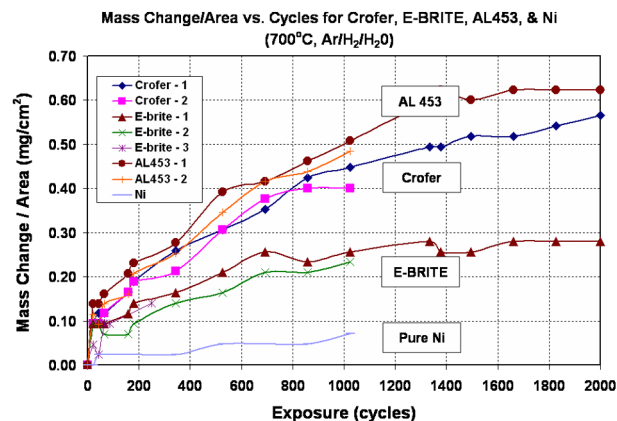


Figure 2. Cyclic Oxidation Data for Ferritic Alloys and Pure Ni Exposed in Simulated Anode Gas (Ar-4%, H_2 , H_2O) at 700°C

Figure 2 is a typical plot of mass change versus time for exposure in simulated anode gas at 700°C.

Exposure in air plus water vapor at 700°C and 900°C resulted in accelerated growth of chromia scales and accelerated oxide spallation from alloys that did not contain a reactive element (e.g. E-BRITE). External layers of $MnCr_2O_4$ were observed to form on Crofer at 900°C. These may result in reduced oxide evaporation. Oxide growth rates were substantially lower at 700°C than at 900°C. Sigma phase was observed to form at 700°C in the alloys with higher chromium concentration, e.g. E-BRITE. Typical microstructures of this alloy after exposure are presented in Figure 3. The sigma phase formation was more extensive in atmospheres containing water vapor. This phase must be avoided since it is very brittle and tends to crack, as indicated in Figure 3.

Task 2: Fundamental Aspects of Thermomechanical Behavior

Indentation testing to determine the fracture toughness of chromia scale/alloy interfaces has been performed on E-BRITE specimens exposed in wet air and simulated anode gas environments at 900°C. Specimens exposed in wet air for 100 hours and longer showed indentation-induced flaking of the chromia scale, indicative of a thin chromia scale and a non-uniform interfacial toughness. The size of the

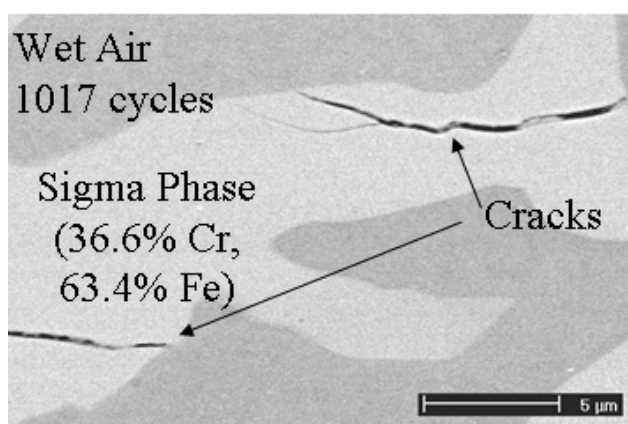
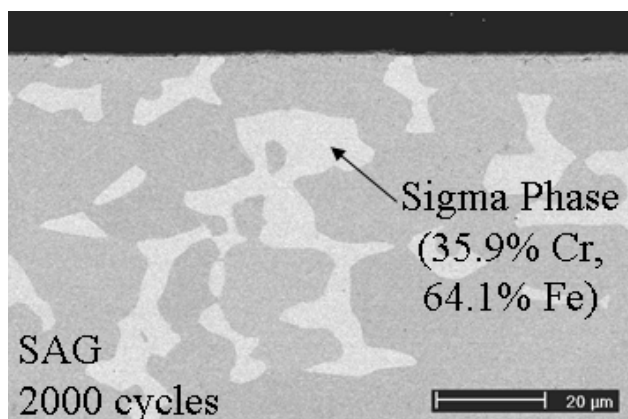


Figure 3. Micrographs Showing Sigma Phase Formation in E-BRITE at 700°C

region experiencing debonding did not change with exposure. This behavior is consistent with weight gain measurements and observations via optical microscopy of spontaneous flaking of chromia scales in these specimens.

Specimens exposed in simulated anode gas showed peeling of a comparatively thick, intact chromia scale (see Figure 1), with an increase in debond size with exposure. This behavior is also consistent with weight gain measurements and observations of a thickening chromia scale remaining attached to the alloy. Fracture mechanics analysis of the indent problem, coupled with residual stresses measured by XRD and oxide thicknesses measured by cross-section SEM, yielded interfacial fracture toughness values for these specimens. Toughness values for a specimen exposed for 364 hours in simulated anode gas and oxide growth data have

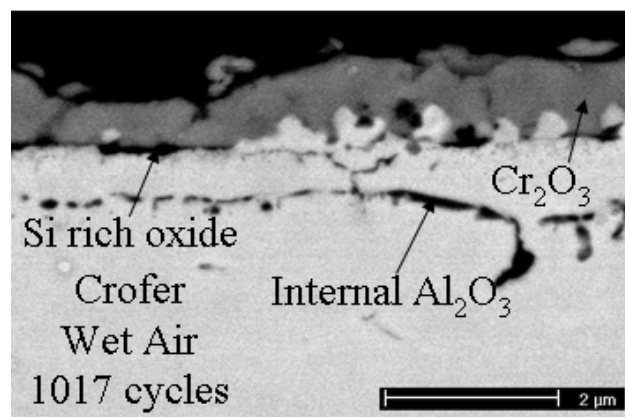
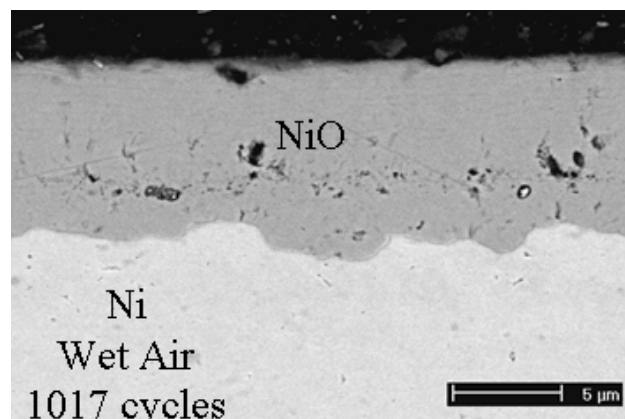


Figure 4. Comparison of Oxide Thickness for NiO and Cr₂O₃ formed at 700°C

been used to predict that spontaneous spallation will occur at approximately 800 hours. This prediction is consistent with observations of specimens exposed for 800 hours and more.

Task 3: Alternative Material Choices

Experiments are being carried out on pure Ni as a possible alternative interconnect material. Figure 2 includes the oxidation data for Ni in the simulated anode gas at 700°C. The Ni did not form an oxide layer in this gas. The small mass gain is believed to result from the dissolution of hydrogen and/or oxygen into the Ni. Figure 4 shows cross-sections of Ni and the ferritic alloys after exposure in moist air at 700°C. The NiO layer is approximately ten times thicker than the layers of Cr₂O₃. However, the NiO has a much higher electrical conductivity, so the actual contribution to the resistance of the system may actually be less for a Ni interconnect.

Conclusions

The aim of this project is to evaluate the chemical and thermomechanical stability of interconnect alloys in simulated fuel cell environments. The oxidation of three ferritic stainless steels has been characterized at both a typical operating temperature (700°C) and, to obtain more rapid results, at an elevated temperature (900°C). X-ray diffraction and indentation fracture testing have been used to characterize the mechanical durability of chromia scales grown on interconnect alloys. In addition to providing insights into mechanisms causing chromia spallation, these test techniques offer an alternative means of accelerating oxidation testing. The understanding gained from these tests will be used to suggest ways to optimize the properties of ferritic alloys. A parallel study is being carried out to evaluate the potential use of alternate interconnect alloys.

FY 2004 Publications/Presentations

1. G. H. Meier, F. S. Pettit, and J. L. Beuth, "Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells," Phase I Topical Report on DOE Award: DE FC26 02NT41578, June 2003.
2. G. H. Meier, "Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells," NETL Workshop on Solid Oxide Fuel Cells, Albany, NY, September 2003.
3. G. H. Meier, "Degradation of Materials in Solid Oxide Fuel Cells," ASM International, Materials Solutions, Pittsburgh, PA, October 2003.
4. J. L. Beuth, "Thermo-Mechanical Testing of SOFC Interconnect Alloy Durability," Materials Solutions, Pittsburgh, PA, October 2003.
5. G. H. Meier, "Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells," NETL Workshop on Solid Oxide Fuel Cells, Boston, MA, May 2004.